

THE INFLUENCE OF THE DISSIPATION OF THE REACTION HEAT ON THE ELECTRON TRANSPORT

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By using the theory of stochastic fluctuation we will attempt to explain the fluctuation of solvent influence on the electron transport. We have treated this problem in the case of weak electron-solvent interaction. This interaction produces a fluctuation of the potential surfaces of the final and initial states of the solute molecules. It was shown how this fluctuation affects the electron transfer.

I. INTRODUCTION

The transfer of electrons from one molecule to another is a very important process in biology. In respiration and photosynthesis the primary action of the energy source is to move electrons in an electron transport chain consisting of electron-transfer molecules. New insights into the mechanism of biological electron-transfer were opened by the discovery that they can sometimes occur at a temperature which is too low for ordinary chemical reactions to take place. The understanding that electron transfer in biological systems involves quantum-mechanical tunneling, came with the discovery that the rate of cytochrome oxidation in chromatium is absolutely temperature independent from 100 to 4 K [1]. A closer examination of the theory shows that nuclear motion usually accompanies it. The temperature independence under the condition of low temperatures may actually show that the nuclei (i. e. whole atoms) are tunneling the barrier of their motion [2-5]. In biological processes the distance between the sites of electron localization can be rather substantial, which leads to small tunneling matrix elements. The vibronic energies can be about two orders bigger. This has led to a belief that most biological electron transfer is nonadiabatic. In the present work we have studied the nonadiabatic electron processes. A stochastic approach to adiabatic electron transfer reaction has been developed by some authors [6-7].

II. GENERAL FORMULATION

We can write the Hamiltonian of the molecules of donor and acceptor, which are surrounded by solvent molecules as follows:

$$H(r, Q, R) = H_0(r, Q) + H_{sib}(R) + H_{in}(r, Q, R) + V(r, Q). \quad (2.1)$$

H_0 , H_{sib} , H_{in} are respectively the Hamiltonians of donor and acceptor molecules, solvent and interaction between solvent and molecules of donor and acceptor. V is the Hamiltonian causing a transition of electron from donor to acceptor. We will assume that the initial state is an eigenstate of H_0 and the transitions to other eigenstates of H_0 are induced by the term V . The initial and final states of a system are characterized in the Born-Oppenheimer approximation by the wavefunctions

$$\Psi_{in}(r, Q) = \Phi_i(r, Q) X_{in}(Q) \quad (2.2)$$

$$\Psi_{fm}(r, Q) = \Phi_f(r, Q) X_{fm}(Q). \quad (2.3)$$

Φ_i , Φ_f are the electronic wavefunctions of the donor and acceptor. X_{in} , X_{fm} are the vibrational wavefunctions. The variables r , Q , R are coordinates of the electron, the nucleus of the subsystem (donor and acceptor) and the coordinates of position and orientation of solvent molecules, respectively. We do not consider explicitly the role of vibrations in the solvent. Explicitly this was done for the polar solvent in [8-11]. Distribution of solvent molecules is not homogeneous and their motions are not in a steady state. Therefore we will treat the solvent classically, with R changing with time t . Ψ_{in} , Ψ_{fm} satisfy the Schrödinger equation

$$H_0 \Psi_{in} = E_{in} \Psi_{in} \quad (2.4)$$

$$H_0 \Psi_{fm} = E_{fm} \Psi_{fm}. \quad (2.5)$$

Under the harmonic approximation for the molecular vibration around the adiabatic potential minimum, the total energy is:

$$E_{in} = E_{in}^0 + (v + 1/2) \hbar \omega. \quad (2.6)$$

We will be working in the approximation of the one accepted mode. X_{in} , X_{fm} are the harmonic wavefunction of vibration

$$X_{in} = \left[\frac{\beta}{\pi^{1/2} 2^n n!} \right]^{1/2} H_n(\beta Q) \exp(-\beta^2 Q^2/2) \quad (2.7)$$

$$X_{fm} = \left[\frac{\beta}{\pi^{1/2} 2^n n!} \right]^{1/2} H_n(\beta(Q - \Delta Q)) \exp(-\beta^2(Q - \Delta Q)^2/2), \quad (2.8)$$

where ΔQ denotes the shift of the origin, H_n is the Hermit polynomial of order n , $\beta = (\mu \omega / \hbar)$, where μ , ω are the effective mass and frequency of the vibrational

mode. We consider that the system is in the time $t = 0$ in the state Ψ_{in} . We intend to find the transition probability that in time t the system will be in the state Ψ_{jm} . This transition probability can be expressed in the form

$$W_{in}^{jm} = |\langle \Psi_{jm} | U(t, 0) | \Psi_{in} \rangle|^2, \quad (2.9)$$

where $U(t, 0)$ is the evolution operator, which can be displayed within the framework of the first order time dependent theory

$$U(t, 0) = \exp\left(-\frac{i}{\hbar} \int_0^t \hat{H}(\tau) d\tau\right) \times \\ \times \left[1 - \frac{i}{\hbar} \int_0^t \exp\left(\frac{i}{\hbar} \int_0^{\tau'} \hat{H}(\tau) d\tau\right) V(t') \exp\left(-\frac{i}{\hbar} \int_0^{\tau'} \hat{H}(\tau) d\tau\right) d\tau'\right], \quad (2.10)$$

where

$$\hat{H} = H_0 + H_{stiv} + H_{int}. \quad (2.11)$$

Here we assume that V is independent of time. We will compute the transition probability

$$W_{in}^{jm} = \frac{1}{\hbar^2} |\langle \Psi_{jm} | V | \Psi_{in} \rangle|^2 \times \\ \times \left| \int_0^t \exp\left[-\frac{i}{\hbar} \int_0^{\tau'} (\dot{E}_{jm}(\tau) - \dot{E}_{in}(\tau)) d\tau\right] d\tau' \right|^2, \quad (2.12)$$

where

$$\dot{E}_{in} = E_{in} + h_i(R(t)) \quad (2.13)$$

$$\dot{E}_{jm} = E_{jm} + h_j(R(t)), \quad (2.14)$$

here

$$h_i(R) = \langle \phi_i | H_{stiv} + H_{int} | \phi_i \rangle \quad (2.15)$$

$$h_j(R) = \langle \phi_j | H_{stiv} + H_{int} | \phi_j \rangle. \quad (2.16)$$

$H_{int} + H_{stiv}$ plays the role of fluctuating the electronic state of the molecules of the subsystem. Since the distances between donor and acceptor are large, the mixing the electronic states is small. Then we adopt only diagonal terms of the Hamiltonian H . We will assume, that the Q dependence of H_{int} is very small and we will use that $H_{int}(\tau, Q, R) = H_{int}(\tau, Q_0, R)$, where Q_0 is the equilibrium coordinate of vibration. As it was said above we will treat the solvent classically, with R changing with time t . We rewrite $h_i(R)$, $h_j(R)$ as follows [12]:

$$h_i(t) = \epsilon_i^0 + W_i(t) \quad (2.17)$$

$$h_j(t) = \epsilon_j^0 + W_j(t). \quad (2.18)$$

where ϵ_i^0 and ϵ_j^0 are constant. $W_i(t)$ and $W_j(t)$ are the fluctuating fields belonging to the potential surfaces of the final and initial states of the solute molecules (donor and acceptor). $W_i(t)$ and $W_j(t)$ satisfy

$$\langle W_i(t) \rangle_{stiv} = \langle W_j(t) \rangle_{stiv} = 0, \quad (2.19)$$

where $\langle \quad \rangle_{stiv}$ is the ensemble average over the solvent motion. Under the treatment the transition probability reduces to

$$W_{in}^{jm} = \frac{1}{\hbar^2} |V_{jm, in}|^2 \times \\ \times \left| \int_0^t \exp\left[-\frac{i}{\hbar} \int_0^{\tau'} (\epsilon_{in, jm} + \epsilon(\tau)) d\tau\right] d\tau' \right|^2, \quad (2.20)$$

where

$$\epsilon_{in, jm} = E_{in} + \epsilon_i^0 - (E_{jm} + \epsilon_j^0) \quad (2.21)$$

$$\epsilon(\tau) = W_i(t) - W_j(t) \quad (2.22)$$

$$V_{jm, in} = \langle \Psi_{jm} | V | \Psi_{in} \rangle. \quad (2.22a)$$

We will consider only the nonadiabatic processes and since the electron transition rate is considerably slower than the rate of vibrational relaxation, the distribution of vibrational energy level may be regarded as being in equilibrium. The transfer rate for reaction can be given by

$$R_{ij} = \sum_{m, n} \varrho_n W_{in}^{jm}, \quad (2.23)$$

where

$$\varrho_n = \exp(-E_{in}/kT) / \sum_{m=0}^{\infty} \exp(-E_{im}/kT). \quad (2.24)$$

We rewrite the expression for transfer rate in the following form

$$R_{ij} = \frac{2}{\hbar^2} \sum_{m, n} |V_{jm, in}|^2 \varrho_n \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} \exp\left[-\frac{i}{\hbar} \int_{t_1}^{t_2} (\epsilon(\tau)) d\tau\right] \times \\ \times \exp\left[-\frac{i}{\hbar} [(n+1/2)\hbar\omega - (n+1/2)\hbar\omega + E_0](t_2 - t_1)\right] dt_1, \quad (2.25)$$

where

$$E_0 = E_i^0 + \epsilon_i^0 - E_j^0 - \epsilon_j^0. \quad (2.26)$$

The energy $E_0 + \epsilon(\tau)$ is called the reaction heat and $\epsilon(\tau)$ is a fluctuation of the reaction heat. Assuming the Gauss processes for the fluctuation of the solvent, we obtain

$$R_{ij} = \frac{2}{\hbar^2} \sum_{m,n} |V_{j,m,i}|^2 \theta_n \text{Re} \int_0^t dt_2 \int_0^{t_2} \xi(t_2 - t_1) \times \exp \left[-\frac{i}{\hbar} [(n+1)\hbar\omega - (m+1)\hbar\omega + E_0](t_2 - t_1) \right] dt_1, \quad (2.27)$$

where

$$\xi(t_2 - t_1) = \exp \left[-\frac{1}{\hbar^2} \int_{t_1}^{t_2} \int_{t_1}^{t_2} \langle \epsilon(t_3)\epsilon(t_4) \rangle_{s(t_0)} dt_3 dt_4 \right]. \quad (2.28)$$

We assumed that the process is stationary with the correlation function

$$\langle \epsilon(t_3)\epsilon(t_4) \rangle_{s(t_0)} = \langle \epsilon^2 \rangle_{s(t_0)} \exp[-|t_3 - t_4|/\tau_e] \quad (2.29)$$

$$\langle \epsilon(t) \rangle_{s(t_0)} = 0, \quad (2.29a)$$

where τ_e is the correlation time and $\langle \epsilon^2 \rangle_{s(t_0)}$ is the mean square fluctuation of the reaction heat. Integrating with t_3 and t_4 in eq. (2.26) one obtains

$$\xi(\tau) = \exp[-\Gamma_e(\tau - \tau_e)(1 - \exp[-\tau/\tau_e])]. \quad (2.30)$$

We note

$$\Gamma_e = \frac{1}{\hbar^2} \langle \epsilon^2 \rangle_{s(t_0)} \tau_e. \quad (2.30a)$$

We suppose that we can use the Condon approximation according to which $V_{j,m,i}$ can be factorized.

$$\langle \psi_{j,m} | V | \psi_{i,n} \rangle = \langle \phi_j | V | \phi_i \rangle \langle \chi_{j,m} | \chi_{i,n} \rangle \quad (2.31)$$

$\langle \phi_j | V | \phi_i \rangle$ is taken at the nuclear coordinates, where its value is maximum [10].

$$R_{ij} = \frac{2}{\hbar^2} \sum_{m,n} \theta_n F_{mn} |\langle \phi_j | V | \phi_i \rangle|^2 \text{Re} \int_0^t dt_2 \int_0^{t_2} \xi(t_2 - t_1) \times \exp \left[-\frac{i}{\hbar} [(n+1)\hbar\omega - (m+1)\hbar\omega + E_0](t_2 - t_1) \right] dt_1, \quad (2.32)$$

where $F_{mn} = |\langle \chi_{j,m} | \chi_{i,n} \rangle|^2$. Now we use the relation [13]

$$Z(s, q) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} s^m q^n F_{mn} = [(1-s^2)(1-q^2) + (s-q)^2]^{-\frac{1}{2}} \exp \left(-\frac{\Delta^2(1-s)(1-q)}{(1+s)(1-q) + (1-s)(1+q)} \right), \quad (2.33)$$

where $\Delta^2 = m\omega(\Delta Q)^2/\hbar$ is the dimensionless shift of the origin. For transfer rate we get

$$R_{ij} = \frac{2}{\hbar^2} V^2 \text{Re} \int_0^t dt_2 \int_0^{t_2} \xi(t_2 - t_1) \times \exp \left[-\frac{i}{\hbar} E_0(t_2 - t_1) \right] dt_1, \quad (2.34)$$

where

$$K(\tau) = \exp[-\Delta^2(\bar{n} + 1/2)] \times \exp \left[\frac{\Delta^2}{2} [(\bar{n} + 1)e^{i\omega\tau} + \bar{n}e^{-i\omega\tau}] \right], \quad (2.35)$$

here $V = |\langle \phi_j | V | \phi_i \rangle|$ and $\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}$. Now we can write for R_{ij}

$$R_{ij} = \frac{2}{\hbar^2} V^2 \text{Re} \int_0^t (t - \tau) \xi(\tau) K(\tau) \exp \left[-\frac{i}{\hbar} E_0\tau \right] d\tau \quad (2.36)$$

and for $\Gamma_e t \gg 1$ one can write:

$$R_{ij} = \frac{2V^2}{\hbar^2} t \text{Re} \int_0^{\infty} \xi(\tau) K(\tau) \exp \left[-\frac{i}{\hbar} E_0\tau \right] d\tau. \quad (2.37)$$

Hence one can introduce the rate constant

$$k_{ij} = \frac{2V^2}{\hbar^2} \text{Re} \int_0^{\infty} \xi(\tau) K(\tau) \exp \left[-\frac{i}{\hbar} E_0\tau \right] d\tau. \quad (2.38)$$

Using the multinomial expansion of the $K(\tau)$, we can rewrite eq. (2.38) as

$$k_{ij} = \frac{2V^2}{\hbar^2} \sum_{q=-\infty}^{\infty} \left[\frac{\bar{n} + 1}{\bar{n}} \right]^{q/2} I_q \left[2S[\bar{n}(\bar{n} + 1)]^{1/2} \right] \exp[\Gamma_e \tau_e - S(2\bar{n} + 1)] \times \int_0^{\infty} \exp[-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]] \cos[(E_0/\hbar\omega - q)\omega\tau] d\tau, \quad (2.39)$$

where $S = \Delta^2/2$, I_q is the modified Bessel function. When $\Gamma_e \ll \omega$, we can write eq. (2.39) in the form

$$k_{ij} = \frac{2V^2}{\hbar^2} \left[\frac{\bar{n} + 1}{\bar{n}} \right]^{p/2} I_p \left[2S[\bar{n}(\bar{n} + 1)]^{1/2} \right] \exp[\Gamma_e \tau_e - S(2\bar{n} + 1)] \times \int_0^{\infty} \exp[-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]] d\tau, \quad (2.40)$$

where $p = E_0/\hbar\omega$. A useful expression for k_{ij} may be derived in terms of the confluent hypergeometric function. Upon changing the integration variable to

$$y = 1 - \exp(-\tau/\tau_e)$$

we get

$$k_{ij} = \frac{2V^2}{\hbar^2 \Gamma_e} \left[\frac{\bar{n} + 1}{\bar{n}} \right]^{p/2} I_p \left[2S[\bar{n}(\bar{n} + 1)]^{1/2} \right] \exp[-S(2\bar{n} + 1)] \times M(1, \alpha + 1, \alpha), \quad (2.41)$$

where $\alpha = \Gamma_e \tau_e$. $M(\alpha, b, x)$ is the confluent hypergeometric function.

III. POLAR SOLVENT

Now we apply this theory to the polar solvent. We are interested how the classical solvent vibration mode affects the electron transport. We assumed that the solvent interacts only with the subsystem through charge dipole interactions. We can write the interaction Hamiltonian as [14]

$$H_{int}(\mathbf{r}) = \frac{e}{4\pi\epsilon_0} \int \frac{(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \mathbf{P}(\mathbf{r}') d\mathbf{r}' \quad (3.1)$$

$$H_{rio} = \frac{1}{2c\epsilon_0} \int (\mathbf{P}^2 + \frac{1}{\omega_p^2} \dot{\mathbf{P}}^2) d\mathbf{r}, \quad (3.2)$$

here $\mathbf{P}(\mathbf{r}')$ is the polarization at point \mathbf{r}' , $c = 1/\epsilon_{op} - 1/\epsilon_s$ is the well-known Pekar factor, ω_p is a frequency of the solvent mode and e is a charge of the electron. The polarization is caused by the orientation of the dipoles of the solvent molecules. This polarization will be fluctuating due to solvent orientation. In this case we have

$$h_i(t) = \frac{1}{2c\epsilon_0} \int [(\mathbf{P} - c\mathbf{D}_i)^2 + \frac{1}{\omega_p^2} \dot{\mathbf{P}}^2] d\mathbf{r} - \frac{c}{2\epsilon_0} \int [\mathbf{D}_i(\mathbf{r})]^2 d\mathbf{r} \quad (3.3)$$

$$h_j(t) = \frac{1}{2c\epsilon_0} \int [(\mathbf{P} - c\mathbf{D}_j)^2 + \frac{1}{\omega_p^2} \dot{\mathbf{P}}^2] d\mathbf{r} - \frac{c}{2\epsilon_0} \int [\mathbf{D}_j(\mathbf{r})]^2 d\mathbf{r} \quad (3.4)$$

$$h_i - h_j = \frac{c}{2\epsilon_0} \int ([\mathbf{D}_j(\mathbf{r})]^2 - [\mathbf{D}_i(\mathbf{r})]^2) d\mathbf{r} - \frac{c}{2\epsilon_0} \int (\mathbf{D}_j(\mathbf{r}) - \mathbf{D}_i(\mathbf{r}))^2 d\mathbf{r} + \int \delta\mathbf{P}(\mathbf{r}, t) [\mathbf{D}_j(\mathbf{r}) - \mathbf{D}_i(\mathbf{r})] d\mathbf{r} \quad (3.5)$$

where

$$\mathbf{D}_i(\mathbf{r}) = \frac{e}{4\pi} \int \frac{|\Phi_i(\mathbf{r})|^2 (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' \quad (3.6)$$

$$\mathbf{D}_j(\mathbf{r}) = \frac{e}{4\pi} \int \frac{|\Phi_j(\mathbf{r})|^2 (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d\mathbf{r}' \quad (3.7)$$

and

$$\delta\mathbf{P}(\mathbf{r}, t) = \mathbf{P}(\mathbf{r}, t) - c\mathbf{D}_i \quad (3.8)$$

where $c\mathbf{D}_i$ is the equilibrium polarization of the solvent in the initial electronic state. In eq. (2.22) we have

$$\epsilon(t) = \int \Delta\mathbf{D}(\mathbf{r}) \delta\mathbf{P}(\mathbf{r}, t) d\mathbf{r} \quad (3.9)$$

$$\langle \epsilon(t_3) \epsilon(t_4) \rangle = \int \int \Delta\mathbf{D}(\mathbf{r}) \Delta\mathbf{D}(\mathbf{r}') \langle \delta\mathbf{P}(\mathbf{r}, t_3) \delta\mathbf{P}(\mathbf{r}', t_4) \rangle d\mathbf{r} d\mathbf{r}' \quad (3.10)$$

where

$$\Delta\mathbf{D}(\mathbf{r}) = \mathbf{D}_j(\mathbf{r}) - \mathbf{D}_i(\mathbf{r}).$$

We assume that there does not exist a correlation in space and by the fluctuation-dissipation theorem we get [15]

$$\langle \delta\mathbf{P}(\mathbf{r}, t_3) \delta\mathbf{P}(\mathbf{r}', t_4) \rangle = \delta(\mathbf{r} - \mathbf{r}') \frac{k_B T}{\pi} \int \frac{d\omega}{|\epsilon(\omega)|^2} e^{-i\omega(t_3 - t_4)} \quad (3.11)$$

From the Debye theory of dielectric relaxation it follows that the frequency dependence for $\epsilon''(\omega)/|\epsilon(\omega)|^2$ can be expressed by [6]

$$\epsilon''(\omega)/|\epsilon(\omega)|^2 = \omega\tau_e / (1 + \omega^2\tau_e^2) \quad (3.12)$$

where τ_e is $(\epsilon_{op}/\epsilon_s)\tau_D$, and τ_D is the average time for reorientation of the dipoles of the solvent. Then, by substituting (3.12) into (3.11), we obtain for the correlation function of the process

$$\langle \epsilon(t_3) \epsilon(t_4) \rangle = 2k_B T E_p \exp(-|t_3 - t_4|/\tau_e) \quad (3.13)$$

where $E_p = \frac{c}{2\epsilon_0} \int [\Delta\mathbf{D}(\mathbf{r})]^2 d\mathbf{r}$.

$$E_0 = E_i^0 - E_j^0 + \frac{c}{2\epsilon_0} \int ([\mathbf{D}_j(\mathbf{r})]^2 - [\mathbf{D}_i(\mathbf{r})]^2) d\mathbf{r} - E_p \quad (3.14)$$

$$\Gamma_e = \frac{1}{\hbar} 2k_B T E_p \tau_e \quad (3.15)$$

and the rate constant has the form

$$k_{ij} = \frac{V^2}{k_B T E_p \tau_e} \left[\frac{\bar{n} + 1}{\bar{n}} \right]^{p/2} I_p \left[2S[\bar{n}(\bar{n} + 1)]^{1/2} \right] \exp[-S'(2\bar{n} + 1)] \times M(1, \alpha + 1, \alpha'), \quad (3.16)$$

here $\alpha = 2k_B T E_p \tau_e^2 / \hbar^2$, $p = E_0 / \hbar\omega$. Our results are presented in Fig. 1. In the numerical results we take τ_e in the form [6]

$$\tau_e = \tau_{e0} \exp(E_a / kT), \quad (3.17)$$

where E_a is the activation energy of viscosity. Results are presented as plots of the rate constant k versus temperature.

IV. LIMITING CASES

The expression (3.16) has to be evaluated numerically. In this subsection, we consider several limiting cases where that expression can be simplified.

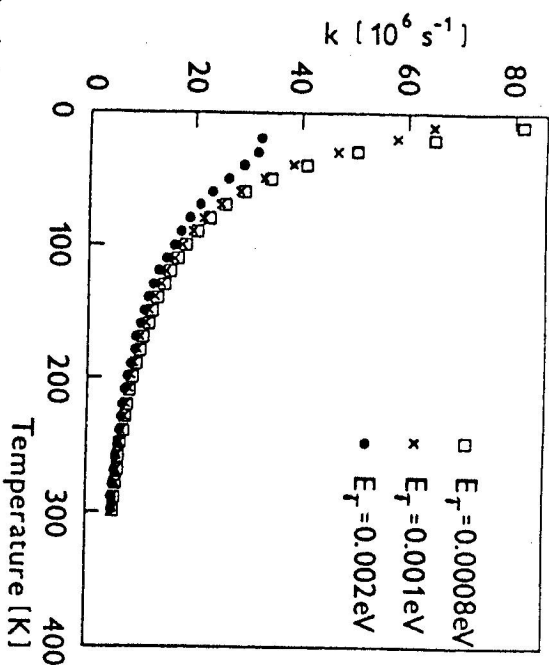


Fig. 1. The electron-transport rate k as a function of temperature. The activationless regime parameters are $p = S = 20$. The vibrational mode frequency $\omega = 6 \times 10^{13} \text{ s}^{-1}$. The other parameters are $E_p = 10^{-5} \text{ eV}$, $V = 10^{-6} \text{ eV}$, $\tau_{e0} = 10^{-13} \text{ s}$.

1. High temperature limit $kT \gg \hbar\omega$.

At very high temperature, $2S[\bar{n}(\bar{n} + 1)]^{1/2}$ becomes large and I_p can be approximated with an asymptotic expression [16]

$$I_p(z) \simeq (2\pi z)^{-1/2} \exp(z - p^2/2z).$$

Substituting this, $(\bar{n} + 1)/\bar{n} \simeq \exp(\hbar\omega/kT)$ and the following high temperature limiting values:

$$2S[\bar{n}(\bar{n} + 1)]^{1/2} - S(2\bar{n} + 1) \simeq -S\hbar\omega/4kT \quad \text{and} \quad 2S[\bar{n}(\bar{n} + 1)]^{1/2} \simeq 2SKT/\hbar\omega$$

into eq. (3.2) gives

$$k_{ij} = \frac{2V^2}{\hbar^2\Gamma_e} [4\pi SKT/\hbar\omega]^{-1/2} M(1, \alpha + 1, \alpha) \exp\left[-\frac{(E_0 - S\hbar\omega)^2}{4S\hbar\omega kT}\right] \quad (4.1)$$

and we have the classical Arrhenius activation behaviour at high temperature. Here α and τ_e are also temperature dependent. In an activationless case when $E_0 = S\hbar\omega$, the rate constant dependence upon temperature in this limiting case is determined by the effect of the solvent. We also see that the preexponential factor depends on the polarity of the solvent.

2. Low temperature $\hbar\omega \gg kT$.

At very low temperature $\bar{n} \rightarrow 0$

$$I_p(z) = z^p/p!$$

where $z = 2S[\bar{n}(\bar{n} + 1)]^{1/2}$ and for the rate constant we get

$$k_{ij} = \frac{2V^2}{\hbar^2\Gamma_e} M(1, \alpha + 1, \alpha) \exp(-S) S^p \frac{1}{p!}. \quad (4.2)$$

Here the temperature dependence of the rate constant is fully determined by the effect of the solvent.

V. CONCLUSION

The main goal of this theory was to describe the influence of the dissipation of the reaction heat on the temperature dependence of the rate constant. The dissipation of the reaction heat is caused by the interaction of the electron with the low frequency mode of the solvent. We assume that the fluctuations of the solvent are caused by heat fluctuation. In this case the mean dispersion of the reaction heat $\langle \epsilon^2 \rangle_{st0} = 2kT E_p$, where E_p is the 'reorganization' energy of the solvent. For the polar solvent $E_p = (c/2\epsilon_0) \int [\Delta\mathbf{D}(\mathbf{r})]^2 d\mathbf{r}$, here $\Delta\mathbf{D}(\mathbf{r})$ is the change of the electrical induction vector at the transition. The numerical results are obtained in the activationless regime, where the influence of the electron-vibrational coupling on the temperature dependence of the rate constant is minimal. In this case the dynamics of the solvent play an important role. Our results are valid for the temperature for which $\Gamma_e(T) \ll \omega$. When $\omega \simeq 10^{14} \text{ s}^{-1}$, the reorganization energy $E_p < 10^{-4} \text{ eV}$ and τ_e is between 10^{-14} s and several hundred picosecond, the condition $\Gamma \ll \omega$ is fulfilled for all temperature from 10 - 300 K. We can see from Fig. 1 that the rate constant at high temperature is lower than at low temperature. This anomalous dependence of the rate constant upon temperature is caused by the dissipation of the reaction heat. The low frequency mode of polar solvent plays an important role in these effects. It was shown that the dynamics of the low frequency mode of the polar solvent has a strong influence on the electron transfer.

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